

QUARTERLY REPORT

HYDROGEN-OXYGEN ELECTROLYTIC REGENERATIVE FUEL CELLS

by

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1. INTRODUCTION

This report reviews the progress made on the development of a regenerative hydrogen-oxygen fuel cell under NASA Contract 3-2781 during the period of 1 October 1965 through 31 December 1965. The program objective is the development of an electrolytically regenerative, hydrogen-oxygen fuel cell that will be superior in performance to currently available rechargeable batteries. The device under development consists of a cell stack that is utilized as an electrolyzer during charge periods and as a fuel cell during discharge periods. Integral gas storage tanks are used to contain hydrogen and oxygen gas that is generated during charge. Such a device offers advantages in the area of watt-hours-per-pound, high ambient temperature operation, and greater cycle life than that which can be obtained from existing secondary batteries. Phase I consisted of a design development and testing of a nominal 75-watt, 44-watt-hour, 6-cell unit to demonstrate the feasibility of a multicell regenerative device. This phase has been completed. Phase II (as modified) consists of the investigation of the asbestos matrix, electrode combinations to improve cycle life, and the design and development of a 500-watt, 600-watt-hour, 34-cell unit of minimum weight for evaluation as a flight prototype.

2. SUMMARY

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During this period, primary emphasis was placed on the testing of single cells with various electrode structures in order to improve cycle-life capabilities and to obtain a better understanding of the mode of deterioration of cell performance. A new type of fuel cell electrode was developed, consisting of a porous-sintered, carbonyl-nickel plaque that is gold coated prior to platinization. It shows promise of improving cycle-life capabilities. From the results of single-cell tests, it has become apparent that a mode of deteriorating performance caused by impurities or contaminants in the electrolyte and/or asbestos exists. Chemical analysis of asbestos and analysis of causes of discoloration have been initiated. A new, instrumented test setup has been partially completed that will be capable of testing two 6-cell units and 5 single-cell units simultaneously. Included in the instrument package is a digital recording system, a continuous (time-voltage) data system and a continuous manual readout system.

author

3. TECHNICAL DISCUSSION

3.1 Single-Cell Tests

Twenty-five single-cell tests were conducted during this period to evaluate the performance of various electrode structures. Test results and construction variables of these cells are summarized in Table I. Cell No. 98 consisted of the same electrodes utilized in cells 92 and 97, the results of which were reported in the fifth quarterly report.⁽¹⁾ The oxygen electrode was an American Cyanamid-type electrode employing 9 mg of platinum per cm² with the nickel subscreen gold plated. The electrodes were washed after use in previous tests, and a new asbestos mat was employed. The cell was cycled 30 times on a standard test-cycle charge of 65 minutes at 9 to 10 A and 35 minutes of discharge at 15 to 18 A. During discharge, the voltage dropped after approximately 20 minutes of discharge, indicating a flooding of the electrode. This performance was consistent throughout the first 30 cycles. Thereafter, the currents were reduced to 5 A on charge, and 7.5 to 8 A during discharge to avoid the fall-off in performance previously observed. The cell was cycled continuously for an additional 95 cycles for a total of 125 cycles. During the reduced current cycling, the voltage during discharge reduced slightly. The final electrolyte concentration of the asbestos mat was analyzed to be 33.4 percent. Figure 1 shows the voltage performance of the cell at various cycles.

Cell No. 99 consisted of oxygen and hydrogen electrodes of the EOS type fabricated of platinized porous nickel plaques. The cell was assembled and put on a standard test cycle of 65 minutes charge, 35 minutes discharge as a control. It was cycled continuously for 100 times during which the discharge performance showed a very slight degradation. The mat from this cell was removed and saved for the purpose of determining effects in the asbestos. The performance data are shown on Fig. 2.

TABLE I
SUMMARY OF SINGLE-CELL TESTS

Cell No.	O ₂ Electrode No.	O ₂ Electrode Catalyst	H ₂ Electrode No.	H ₂ Electrode Catalyst	Mat Thick (In.)	Mat Dry Wt (gm)	Electrolyte % KOH	Electrolyte Wt (gm)	Comments	Results
98		9 mg Pt/ cm ²	215	20 mg Pt/ cm ²	0.060	27.1	39.9	31	Oxygen electrode Cyanamid	125 cycles 30 at high rate, 95 at low rate
99	216	20 mg Pt/ cm ²	206	20 mg Pt/ cm ²	0.060	27.2	39.9	31.1		100 cycles. Showed good performance
100	2 ea.	9 mg Pt/ cm ²	215	20 mg Pt/ cm ²	0.060	27.0	39.9	31.1		60 cycles sensitive to water content
101	2 ea.	9 mg Pt/ cm ²	215	20 mg Pt/ cm ²	0.060	27.1	39.9	31.0		15 cycles. Same performance as cell 100
102		20 mg Pt/ cm ²	210	20 Mg Pt/ cm ²	0.060	26.2	39.7	31	O ₂ electrode Ni plaque (gold-coated and platinized)	Cells shorted out after 5 cycles
103	A _U 1	7-10 mg Pt/cm ²	206	20 mg Pt/ cm ²	0.060	28.0	39.7	31		174 cycles degraded gradually
104	-	9 mg Pt/ cm ²	-	9 mg Pt/ cm ²	0.060	27.5	39.7	31		100 cycles degraded gradually
105	A _U 7	7-10 mg Pt/cm ²	-	20 mg Pt/ cm ²	0.060	27.3	39.9	31	Oxygen electrode gold-plated felt metal	Cycled 46 times. Poor performance
106	-	9 mg Pt/ cm ²	-	9 mg Pt/ cm ²	Reused from cell No. 104	Repeat of No. 104				Cycled 46 times. Internal reaction

TABLE I (contd)
SUMMARY OF SINGLE-CELL TESTS

Cell No.	O ₂ Electrode No.	Catalyst	H ₂ Electrode No.	Catalyst	Mat Thick (In.)	Mat Dry Wt (gm)	Electrolyte % KOH	Electrolyte Wt (gm)	Comments	Results
107	A _U 6	7-10 mg Pt/cm ²	206	20 mg Pt/cm ²	0.060	27.1	39.7	31	Porous nickel plaque (gold-coated and platinized)	Cycled 42 times. Fair performance. Internal reaction during weekend
108	A _U 6	11	206	20 mg Pt/cm ²	0.060	27.1	39.7	31	Repeat of Cell No. 107	Cycled 6 times. Internal short. Good performance
109	A _U 4	Porous-sintered Ni plq. coated and plat. by Bishop 20 mg Pt/cm ²	-	20 mg Pt/cm ²	0.060	27.4	39.7	31		Cycled 44 times. Fair performance. Gradual degradation
110	A _U 5	Ni-felt mtl. plq. gold-coated and plat. by Bishop 20 mg Pt/cm ²	-	20 mg Pt/cm ²	0.060	28.0	39.7	31.0		Cycled 50 times. Fair performance
111	A _U 3	" " Bishop	-	20 mg Pt/cm ²	0.060	28.0	39.7	31.0		Different pressure. Transducer failed

TABLE I (contd)
SUMMARY OF SINGLE-CELL TESTS

Cell No.	O ₂ Electrode Catalyst	H ₂ Electrode No.	Electrolyte % KOH	Mat Thick (In.)	Mat Dry Wt (gm)	Electrolyte Wt (gm)	Comments	Results
112	A _u ⁴	-	20 mg Pt/cm ²	0.060	27.6	31.0	Repeat of Cell No. 109	Cycled 18 times. Poor performance
113	A _u ⁶	206	20 mg Pt/cm ²	0.060	27.0	31.0		78 cycles
	Porous Ni plq. gold-coated plat. 7-10 mg Pt/cm ²							
114	A _u	"	Porous Ni plq. No catalyst	0.060	27.0	39.7	31.0	Just changed cell to see effect of Ni on asbestos
115	-	20 mg Pt/cm ²	20 mg Pt/cm ²	0.060	27.1	39.7	31.0	8 cycles. Very poor performance
							1 layer of cellophane on hydrogen electrode	
116	A _u ⁴	7.5 mg Pt/cm ²	208	20 mg Pt/cm ²	12.0	39.7	35.0	1 cycle. Cell shorted
			layers Webril 1 layer cellophane					

TABLE I (contd)
SUMMARY OF SINGLE-CELL TESTS

Cell No.	O_2 Electrode Catalyst	H_2 Electrode No.	Electrode Catalyst	Mat Thick (In.)	Mat Dry Wt (gm)	Electrolyte % KOH	Wt (gm)	Comments	Results
117	A _u 12	7.5 mg Pt/cm ²	216	20 mg Pt/cm ²	0.060	26.8	39.7	31.0	121 cycles. Good initial performance degraded slowly
118	A _u 10	7.5 mg Pt/cm ²	217		0.060	27.2	39.7	31.0	Oxygen electrode felt metal substrate
119	Am Cy	9 mg Pt/cm ²	Am Cy	9 mg Pt/cm ²	0.060	27.1	39.7	31.0	61 cycles. Gradual degradation
120	Am Cy	9 mg Pt/cm ²	Am Cy	9 mg Pt/cm ²	0.060	27.2	39.7	31.0	50 cycles. Gradual degradation
121	(Same as Cell 120)								Repeat of Cell No. 120 with washed O_2 electrode
122	(Same as Cell 120)								Repeat of Cell No. 119 with washed O_2 electrode
123	(Same as Cell 120)								Repeat of Cell No. 121 with washed H_2 electrode
124	(Same as Cell 120)								Repeat of Cell No. 122 with washed H_2 electrode



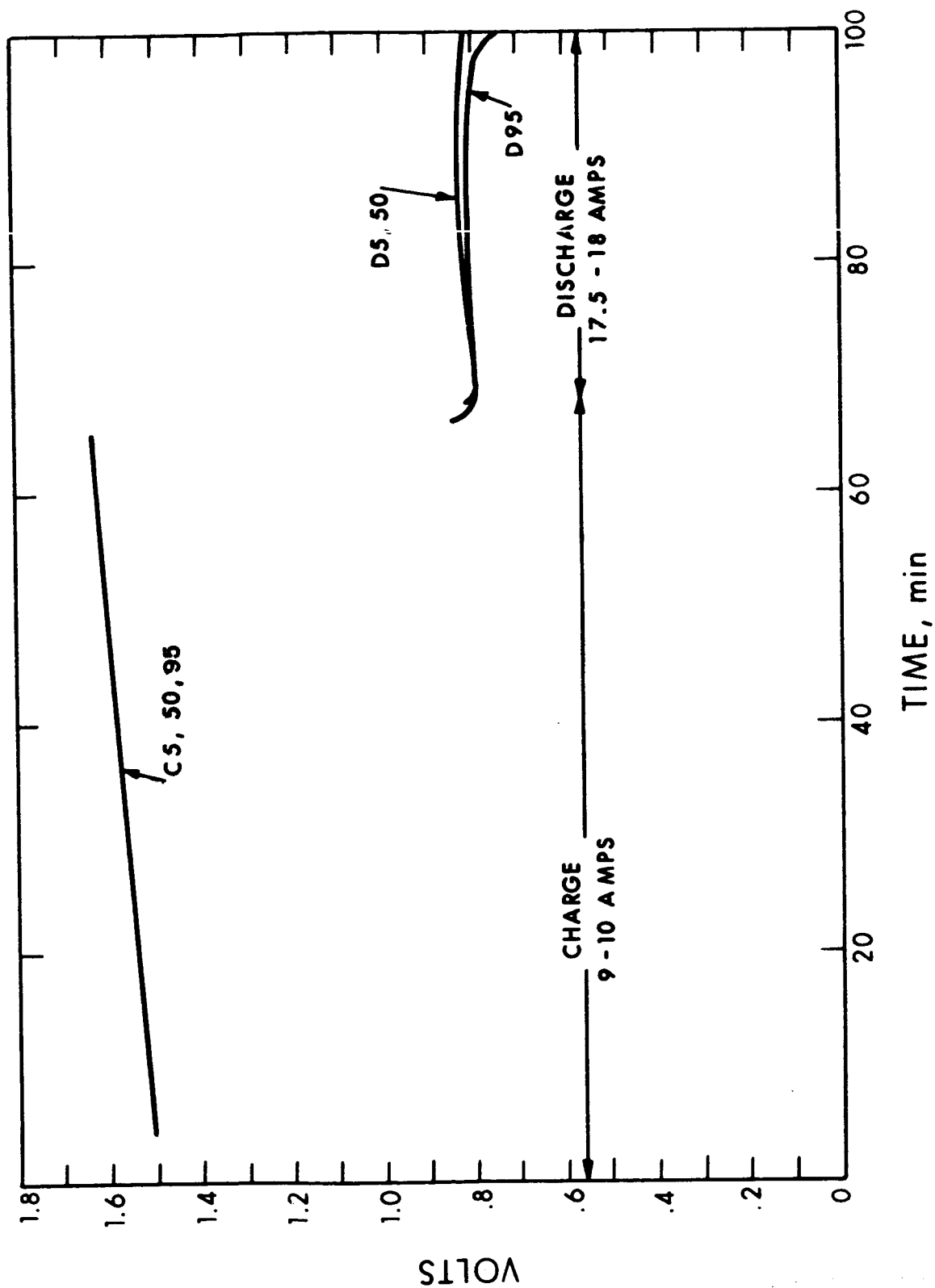


FIG. 2 CYCLING PERFORMANCE OF CELL NO. 99

Cell No. 100 consisted of two Cyanamid 9 mg platinum per cm² (gold-plated nickel screen) electrodes back to back on the oxygen side and a standard EOS platinized nickel plaque on the hydrogen side. Purpose of the test was to determine if the back-to-back oxygen electrodes would reduce the sensitivity to water content, i.e., flooding out and drying observed with American Cyanamid electrodes when used in the regenerative fuel cell. The cell was cycled continuously for 60 times on the standard cycle. A typical cycle is shown in Fig. 3. As can be seen, even with the back-to-back oxygen electrodes, the cell exhibited a gradual rise in voltage at the end of charge (indicating drying out, a dip in the voltage initially during discharge, and rapid fall-off in voltage toward the end of discharge (indicating flooding). However, during the middle of discharge, the performance of these electrodes was excellent.

Cell No. 101 was a repeat of the previous cell No. 100 utilizing the same electrodes after they had been washed and employing a new asbestos mat. The performance of the cell was virtually identical to the previous cell, and the test was stopped after 15 cycles.

Cell No. 102 consisted of a standard porous nickel plaque 20 mg platinum per cm² hydrogen electrode and a new type of oxygen electrode. This oxygen electrode was fabricated at EOS by gold plating and then platinizing a standard porous nickel plaque.

The procedure used in preparing these new electrodes is similar to that used in fabricating our standard type. The steps are as follows:

1. Plaques are washed and degreased.
2. A hot (190-200°F) electroless gold plating solution is continuously recycled through the plaque. The plating solution is a commercial material designated Auroelectroless-N, manufactured by Lee Ronal, Inc. It contains 1 troy ounce of gold per gallon. 400 cc of this solution is used per 6-inch-diameter electrode and contains 3.3 grams of gold.

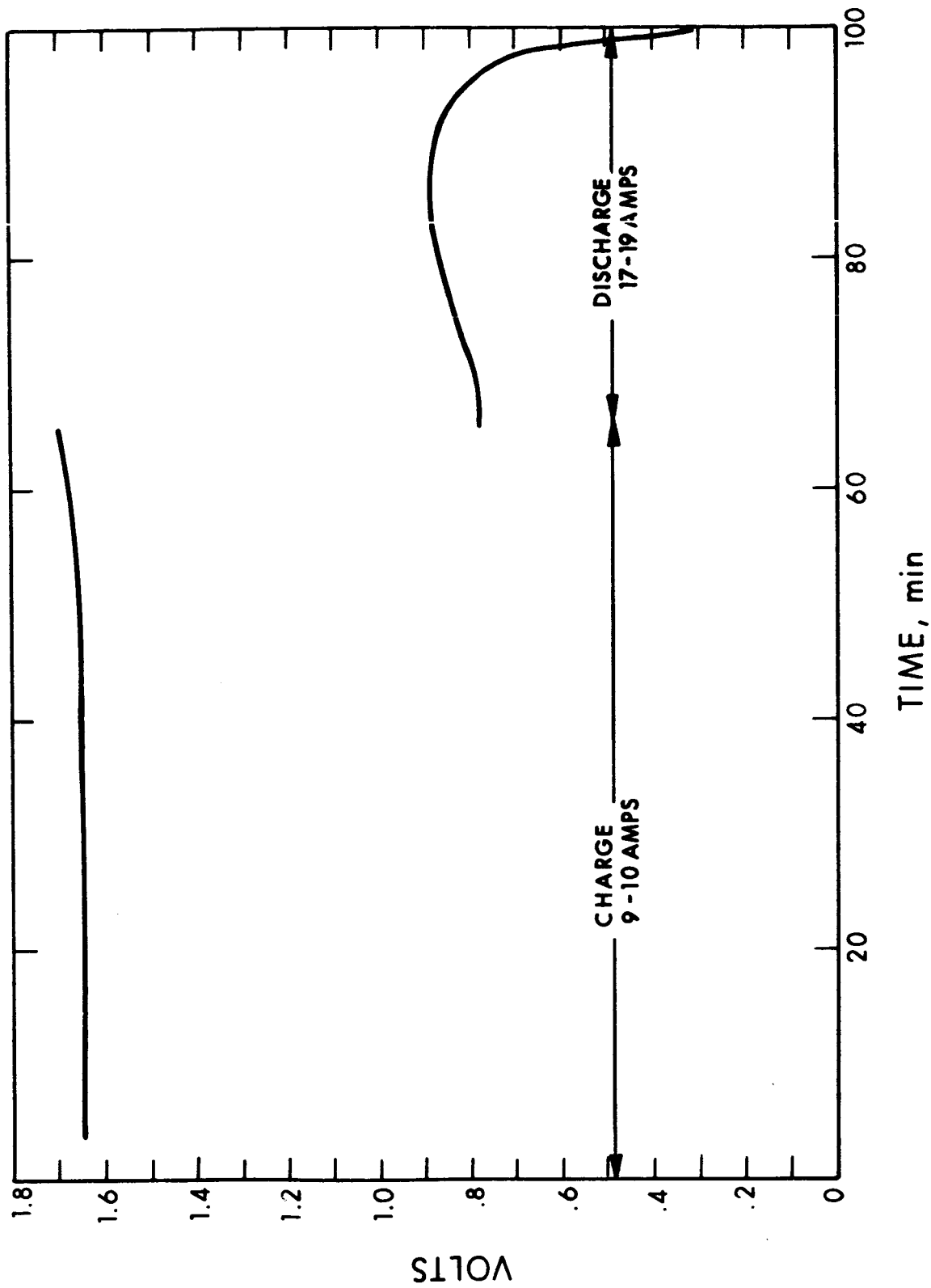


FIG. 3 PERFORMANCE DATA OF TWO CYANAMID ELECTRODES BACK-TO-BACK AS OXYGEN ELECTRODES

3. After removal from the electroless bath, the electrodes are washed and then immersed in a gold cyanide electroplating bath. An electroplating of an additional 3.7 grams of gold is then put on the electrodes.
4. After removal from the gold electroplating bath, the electrodes are washed and immersed in a chloroplatinic acid plating bath. Platinum is plated on the electrode to an equivalent of 7.5 mg/cm^2 .

Cell No. 102 was cycled 5 times and then developed an internal short. It was disassembled and examined. The short was found on the edge of the electrodes and was due most probably to poor assembly. The electrodes were washed, assembled with a new asbestos mat, and designated cell No. 103. The performance of this cell at various cycles is presented in Fig. 4. As can be seen, during the first 150 cycles, only slight degradation was encountered; however, beyond that point a rapid rate of degradation was observed. Examination of the disassembled cell revealed no obvious cause for the degradation. This cell represented our initial attempt at fabricating such electrodes. It demonstrated that this approach is promising and warrants further study and perfection.

Cell No. 104 was installed with American Cyanamid H_2 and O_2 electrodes having $9 \text{ mg platinum per cm}^2$ on gold-plated nickel screens. This test was set up to determine effects that occur in the asbestos without "free" nickel being present in the electrodes. The cell was cycled 100 times, during which a gradual degradation in performance was observed. The electrodes were then removed from the cell, washed, and replaced in the cell utilizing the same asbestos mat. This cell was designated No. 106. The performances during various cycles of cells No. 104 and 106 are presented in Fig. 5. As can be seen, washing the electrodes and rebuilding the cell improved performance somewhat. The improvement in performance by rebuilding of the cell is inconclusive. It does, however, indicate the possibility of a water soluble

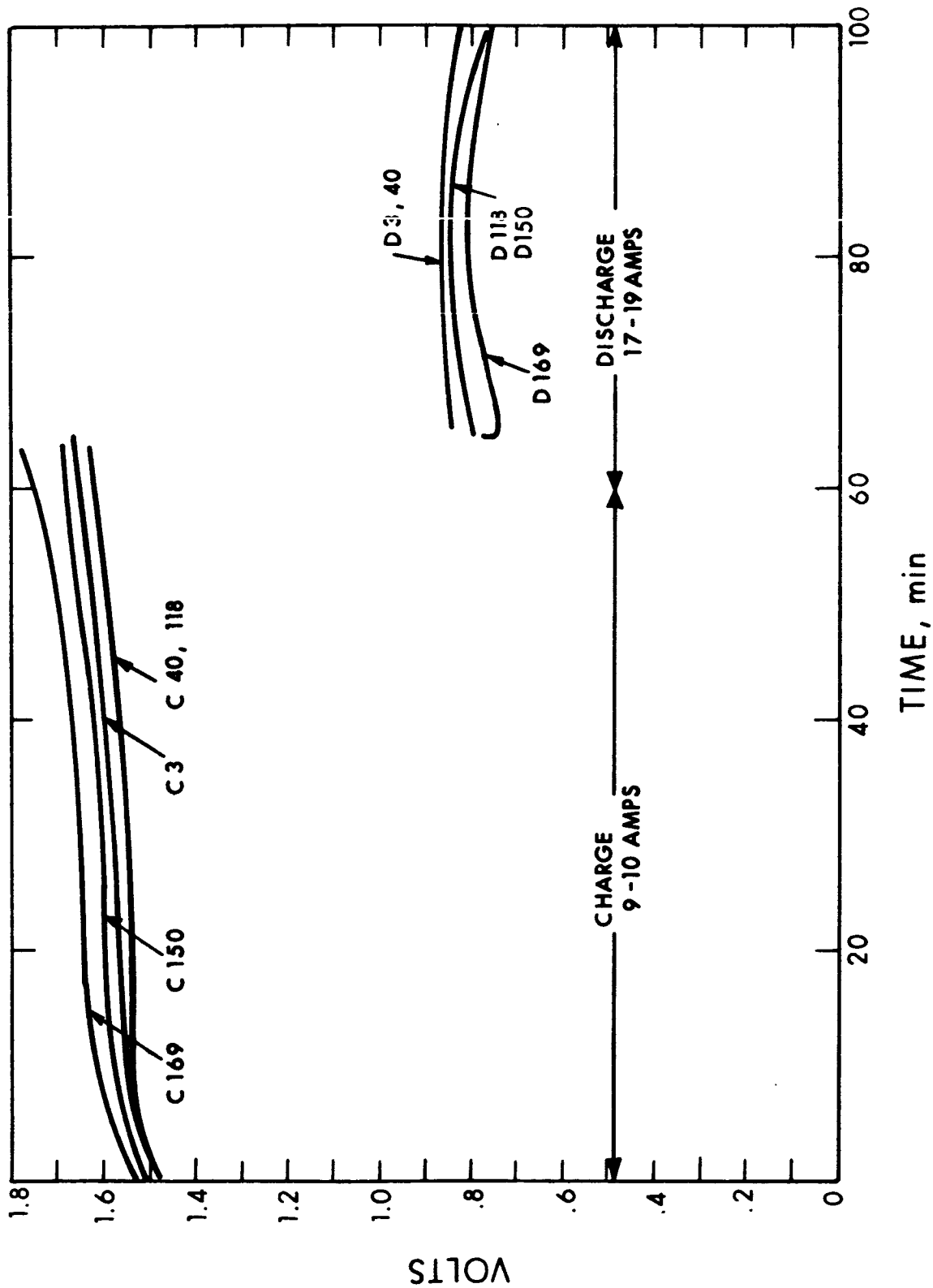


FIG. 4 CYCLING PERFORMANCE OF CELL NO. 103

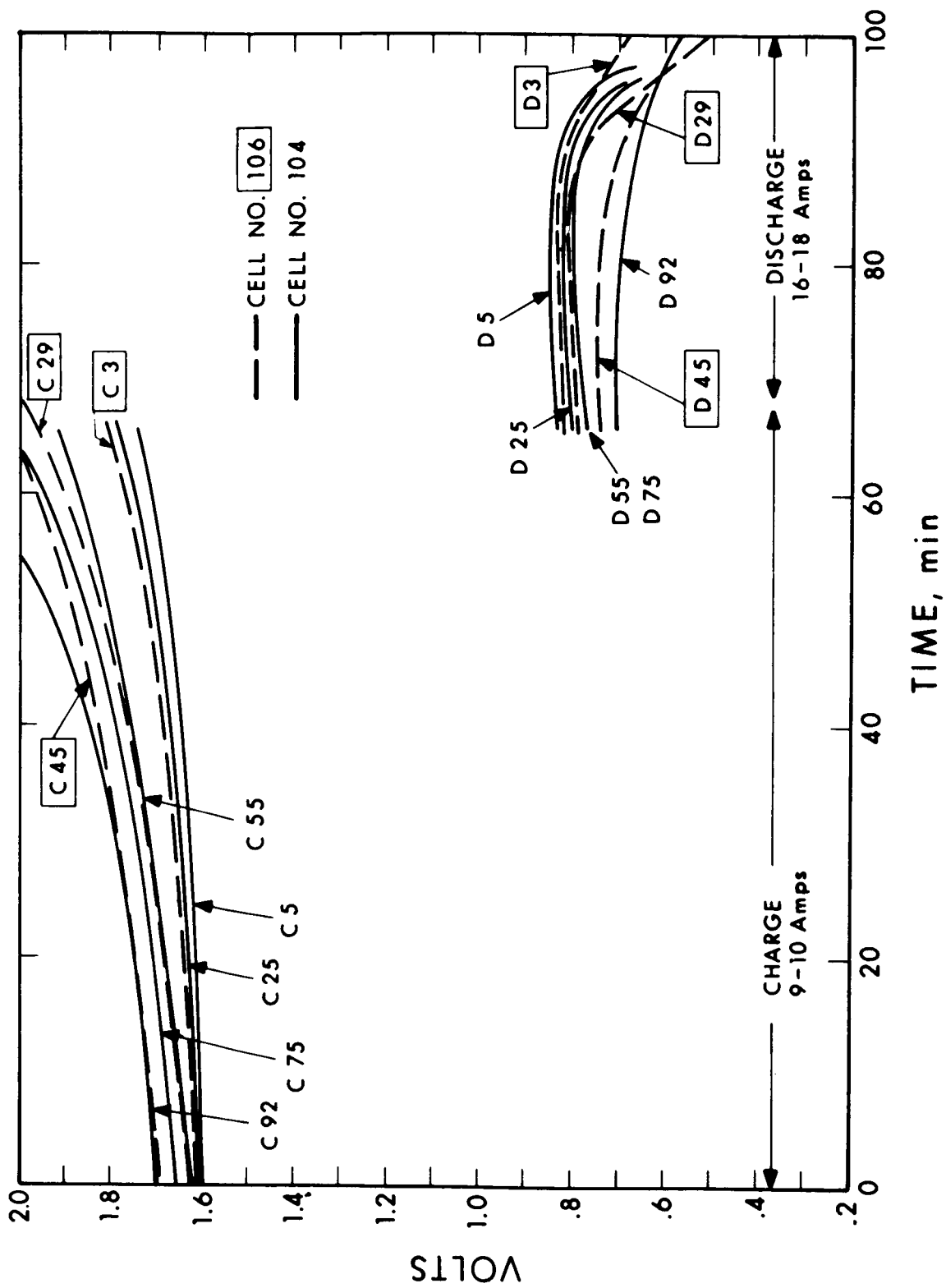


FIG. 5 CYCLING PERFORMANCE OF CELL NOS. 104 AND 106

catalyst poison, which accumulated on the electrodes with cycling, as the cause of gradual performance degradation. Cell No. 106 also degraded gradually as shown in Fig. 5.

Cell No. 105 consisted of an oxygen electrode similar to the type used in cell 103 with the exception that the electrode substrate was nickel felt metal as opposed to the sintered porous nickel plaque. This cell was cycled 46 times and showed relatively poor performance, discharging at approximately 0.7 of a volt per cell and charging in a range of 1.65 to 1.9 volts.

Cell No. 107 consisted of an oxygen electrode processed similarly to the electrode used in cell No. 103, i.e., a gold-plated, platinized porous nickel plaque. This cell was cycled 42 times after which an internal reaction occurred within the cell causing a drastic drop in performance.

Electrodes were removed from cell 107 and were washed, reassembled with a new asbestos mat, and designated cell No. 108. This cell was cycled six times, at which time an internal short developed within the cell. The performance data of cells No. 107 and 108 are shown on Fig. 6. As can be seen, performance recovered after the reassembly. Results of the rebuilding of cell No. 107 and the rebuilding of cell No. 103, described previously, seem to indicate that an additional deteriorating factor within the cells exists besides the gradual oxidation of the porous nickel plaques as previously determined. This deterioration may be an impurity that comes from the electrolyte and/or the asbestos mat.

Cells No. 109 and 111 consisted of porous sintered nickel plaques that were gold coated at EOS and platinized by the Bishop Company, utilizing a proprietary platinizing process. Cell No. 109 was cycled 44 times and showed fair performance, discharging at 0.8 to 0.85 volts per cell and charging at 1.5 to 1.6 volts. A gradual increase in the charging voltage and decrease in the discharge voltage was observed through the cycling. Testing was stopped after 44 cycles.

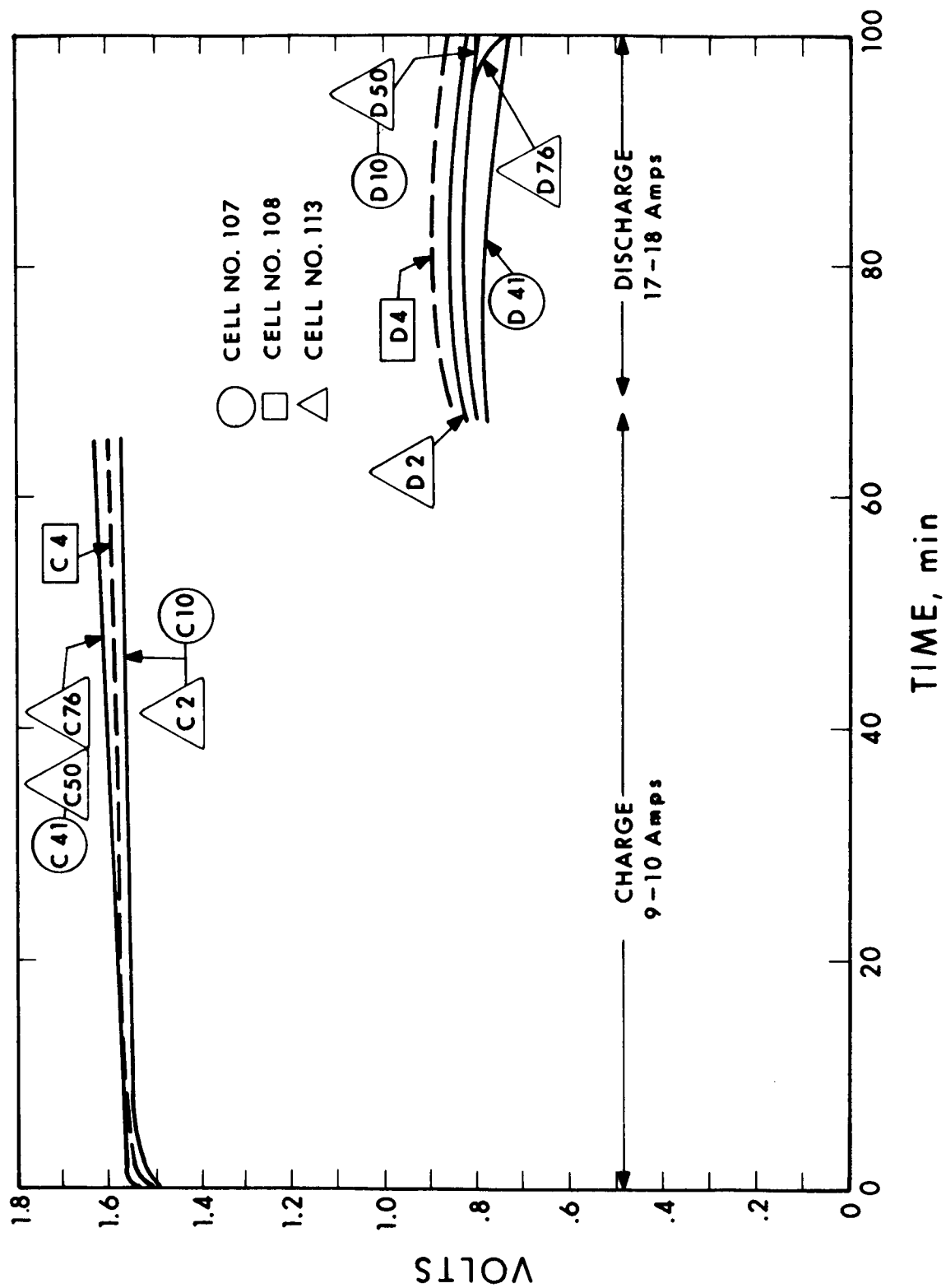


FIG. 6 CYCLING PERFORMANCE OF REWASHED ELECTRODES

Cell No. 111 was not subjected to tests due to failure of the differential pressure transducer during the initial setup.

Cell No. 110 consisted of a felt metal nickel plaque that was gold coated at EOS and platinized by the Bishop Company. This cell was cycled 50 times and then the test was discontinued. Performance of the cell was poor. At end of discharge, there was a rapid fall-off in voltage, and, at end of charge, there was a substantial rise in voltage.

Poor performance obtained from cells No. 105 and 110, employing nickel felt metal substructures, was disappointing and very different from results obtained with prior cells utilizing nickel felt metal samples obtained from the NASA contract monitor. Discussions held with technical representatives of Huyck Corporation revealed that there are two types of fiber structures, i.e., A10 and A30. The electrodes from cells No. 105 and 110 employed A30 type fibers. The A10 fiber structures have a larger surface area and thus presumably a more active electrochemical area. It was therefore suggested that the original sample may have been the A10 type. It was also suggested that different densities of felt metal be evaluated as another variable. (All the previous work has been done with 15 percent dense nickel felt metal.) Based on these discussions, orders will be placed for felt metal of different densities and both fiber designations.

Cell No. 112 was a repeat of cell No. 109, utilizing the same electrodes after they had been washed with a new asbestos mat. The cell was cycled 18 times. The initial performance was considerably improved over the performance obtained during the latter cycles in cell No. 109, once again demonstrating the ability of rejuvenating the cell by washing the electrodes and utilizing a new asbestos mat.

Cell No. 113 was a repeat run using the electrodes from cells 108 and 107 after they were washed, plus a new mat. This cell was cycled continuously 78 times. The data and performance of this cell is also presented in Fig. 6. Once again, the cell performance recovered initially in a new assembly and gradually degraded.

The current series of tests with gold-plated electrodes indicates that nickel in the electrode structure is not the only cause of cell performance deterioration. A series of tests was therefore initiated to determine what aspects of the mat and/or electrolyte were causing the degradation.

Examination of multi- and single-cells tested has consistently shown a gray-black discoloration of the asbestos mat adjacent to the hydrogen electrode. Although cell deterioration is not primarily due to hydrogen electrode failure, it is felt that this discoloration may be the end product of some anodic reaction in the electrolyte and/or mat. If this is the case, the oxygen electrode could be expected to be affected by the concurrent cathodic reaction.

Several tests, including cell No. 111, have been aborted during the first cycle. It has been noted on these occasions that the gray discoloration occurs principally as the result of the charge mode of operation. Therefore, emphasis was placed on testing using cells in the electrolysis mode.

Preliminary chemical analyses of the discoloration zone in the mat (described in detail in Subsection 3.2) show that platinum is a principal constituent of the discolored zone. Since platinum in the mat near the anode could not readily be conceived as the cause of cathode deterioration, other cause and effect systems were investigated. In order to eliminate possible effects of anode platinum, cell No. 114 was assembled with a non-gold-plated, non-platinum-catalyzed nickel plaque on the hydrogen side. This cell was subjected to charging at 10 amperes for approximately one hour, after which it was disassembled and examined. A slight gray discoloration adjacent to the anode was noted. This test indicated that platinum is not the only factor in the asbestos discoloration.

The next test, cell No. 115, was made to see if a semi-permeable barrier between the anode and the mat would stop formation of the gray-black deposit. The cell contained standard EOS type

electrodes with a conventional asbestos mat, plus one layer of battery separator cellophane placed between the mat and the hydrogen electrode. The addition of the cellophane layer increased cell resistance appreciably and the cell could only be cycled at reduced current levels, i.e., approximately 5 amperes during charge and 10 amperes during discharge. The cell was cycled in such a manner for eight cycles and then disassembled. It was observed that there was virtually no discoloration of the cellophane or the asbestos mat adjacent to the hydrogen electrode, indicating that the discoloration had been stopped by the cellophane.

Several interpretations of this test result are possible. It was obvious that the cellophane provided a barrier for the migration of particles from the anode to the mat. However, the question of whether such particles originate in the electrode structure or are the reaction products from interactions between the electrode and ionized materials in the mat remained. In order to eliminate one of these variables, several cells were assembled with Webril mats of varying thicknesses in place of the standard fuel cell grade asbestos. As anticipated, cells employing just Webril mats could not withstand minor differential pressures and were, therefore, not subjected to test.

Cell No. 116 consisted of two layers of Webril with one layer of cellophane in the center to enable the cell to hold a pressure differential. This cell was cycled once, after which it developed an internal short, probably due to a wire whisker protruding from the edge of one of the electrodes. No discoloration was noted on the Webril when the cell was disassembled. This test will be repeated to confirm the results over a longer cycle period. If confirmed, it will be a positive indication that the gray-black deposits are in part due to asbestos or electrolyte impurities.

Cell No. 117 consisted of a gold-coated platinized oxygen electrode, as previously described, with the exception that after

the gold coating (and prior to the platinization) the electrode was fired in a hydrogen furnace for one hour at 1500^oF. This firing was added to the electrode preparation procedure in an attempt to improve the adherence of the gold coating to the nickel substrate. The firing had the effect of essentially diffusing and alloying the gold layer into the upper surfaces of the nickel plaque. After removal from the furnace, the plaque surface had changed from a dull gold color to a gray nickel color with a slight yellow tinge. The hydrogen electrode employed in the cell was a standard EOS type 20 mg platinum per cm² electrode. The cell was put on a standard cycle and subjected to 121 continuous cycles. It showed good initial performance with a gradual degradation similar to that obtained in previous tests with cells employing gold-coated platinized porous nickel electrodes (as, for example, cell No. 103).

Cell No. 118 consisted of an oxygen electrode processed similarly to cell No. 117 with the exception that the porous substrate was nickel felt metal. This cell was cycled six times and showed relatively poor performance. The test was, therefore, discontinued. Poor performance of this felt metal substrate type electrode was similar to that obtained with cells 105 and 110.

Cells No. 119 and 120 consisted of American Cyanamid hydrogen and oxygen electrodes containing 9 mg of platinum per cm² on a nickel screen that had been gold plated with a minimum of 100 micro-inches of gold to insure a pinhole-free surface. By the use of these type electrodes, it was hoped to eliminate the deteriorations caused by the gradual oxidation of the nickel substrates, observed in some of the earlier work. By the elimination of this variable, it should be possible to obtain a better understanding of the causes of other modes of degradation.

Cell No. 119 was cycled 61 times, then disassembled. The oxygen electrode was removed, washed, and reassembled with the same asbestos mat and hydrogen electrode and designated cell No. 122. This

cell was then cycled four times and disassembled. The hydrogen electrode was washed, reassembled with the same oxygen and asbestos mat, and cycled two additional times. The same procedure was followed in cells No. 121 and 124.

Results of the testing with cells 119, 122, 121, and 124 are shown in Figs. 7 and 8. As can be seen, the initial cell performance was good and with cycling there was a gradual degradation of performance. Washing the oxygen electrode and rebuilding the cell had only a slight effect on improving the performance, and washing of the hydrogen electrode had no beneficial effect. These results are inconsistent with the results obtained from cells No. 104 and 106 in which both electrodes were washed and reassembled with the old asbestos mat. However, these types of tests are difficult to conduct since in the disassembly of the cell, it is possible that water is lost from the asbestos mat and carbonates form in the mat due to CO_2 pickup from the air. The electrodes taken from these cells will be washed and tested again with fresh asbestos mats to obtain further information.

3.2 Asbestos Studies

Asbestos samples taken from the multicell unit serial number 1003-34 (the test results of which were reported in the fifth quarterly report) were submitted to an outside testing laboratory for a semi-quantitative spectrographic analysis. Two samples of used mats were prepared by mixing the asbestos in a blender to obtain a homogeneous mixture. A third sample was prepared utilizing a fresh asbestos mat by homogenizing it with distilled water. The results of the analysis are presented in Table II. The major difference between these and previous test results was the large percentage of calcium found in the asbestos mats. Prior spectrographic analyses showed calcium concentrations in the tenths of a percent range. However, the asbestos material used in these tests represents a new lot of material recently received from Johns-Manville. Possibly there is this variation in the raw material. Two samples of dry asbestos, one from the previous

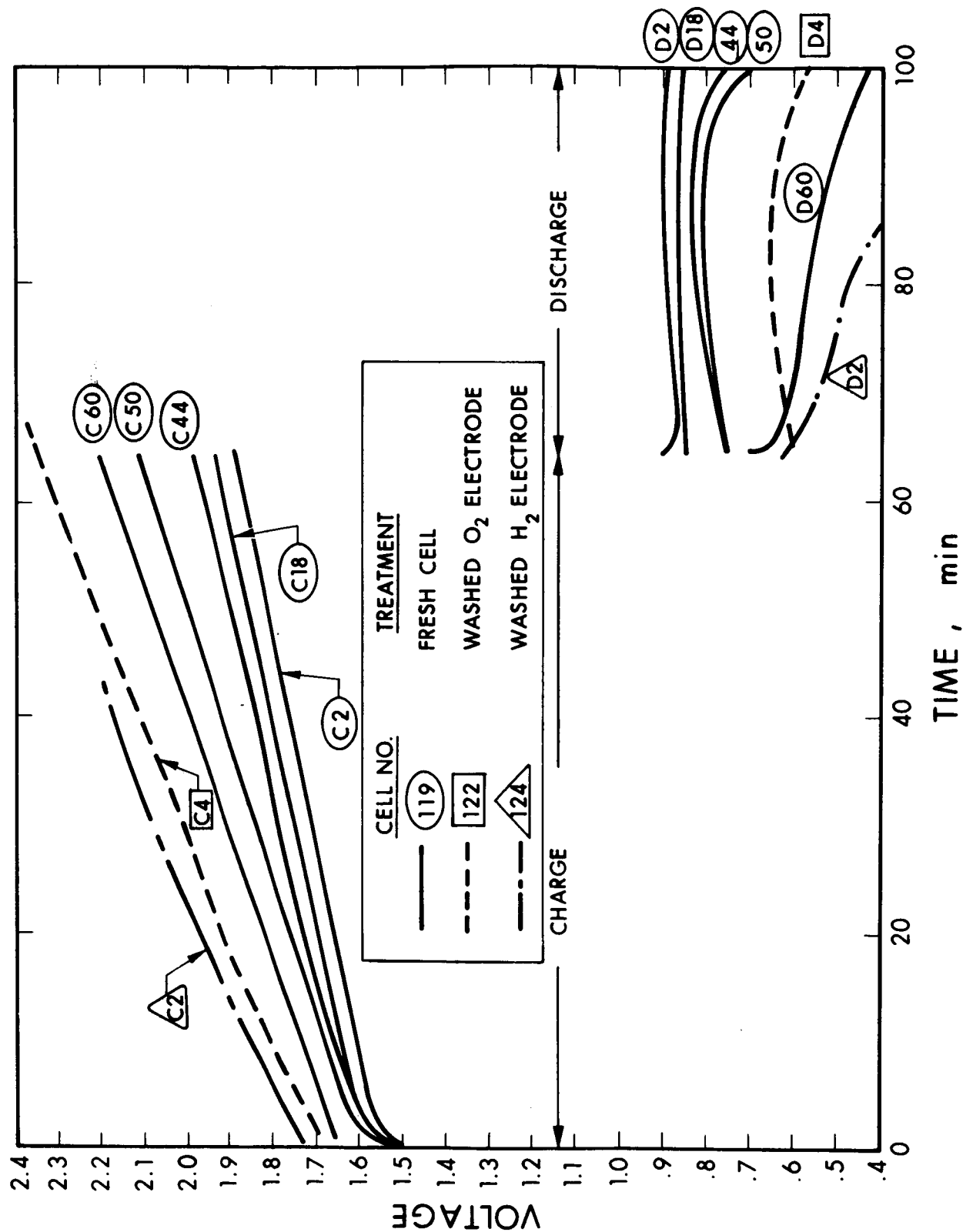


FIG. 7 CYCLING PERFORMANCE WITH WASHED ELECTRODES

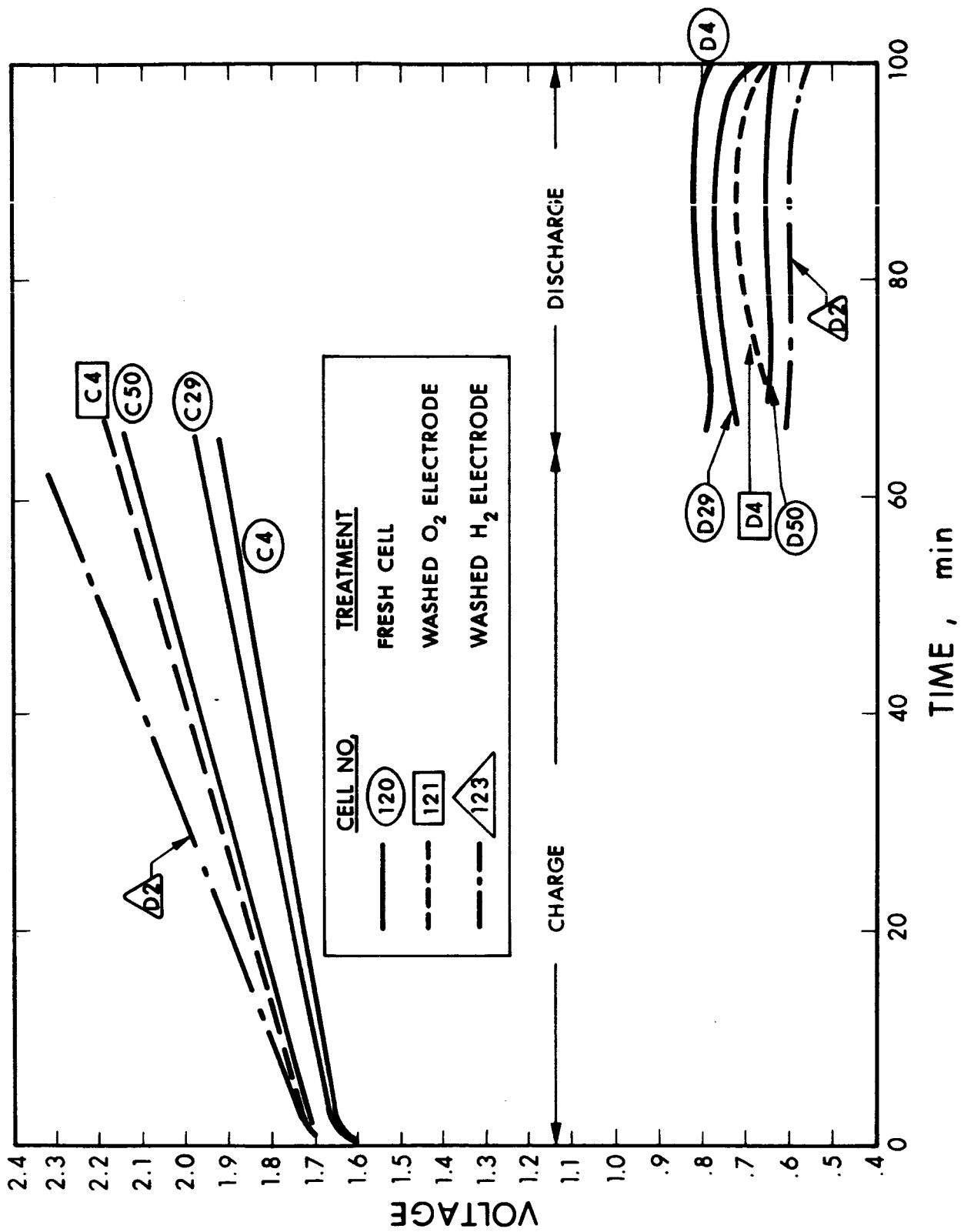


FIG. 8 CYCLING PERFORMANCE WITH WASHED ELECTRODES

TABLE II
ASBESTOS SPECTROGRAPHIC ANALYSIS

	Pure Asbestos Sample (%)	Samples Taken from Fuel Cell S/N 1003-34 (%)	
Ag	0.0005*	0.0005*	0.0005*
Al	0.08	0.09	0.01
As	0.05*	0.05*	0.05*
B	0.01	0.01	0.01
Ba	0.08*	0.08*	0.08*
Be	0.0001*	0.0001*	0.0001*
Bi	0.001*	0.001*	0.001*
Ca	8.5	7.	8.5
Cd	0.05*	0.05*	0.05*
Co	0.007*	0.007*	0.007*
Cr	0.008*	0.008*	0.008*
Cu	0.01	0.02	0.01
Fe	0.2	0.01	0.1
K	Not Detected	Rem.△	Rem.△
Li	0.1*	0.1	0.1*
Mg	21.	15.	5.
Mn	0.04	0.005	0.001
Mo	0.01*	0.01*	0.01*
Na	0.07*	0.15	0.1
Nb	0.01*	0.01*	0.01*
Ni	0.005*	0.05	0.07
Pb	0.007*	0.007*	0.007*
Sb	0.02*	0.02*	0.02*
Si	16.5	8.5	3.5
Sn	0.005*	0.005*	0.005*
Sr	0.01	0.005	0.005
Ti	0.003*	0.003*	0.003*
V	0.005*	0.005*	0.005*
Zn	0.1*	0.1*	0.1*
Zr	0.003*	0.003*	0.003*
Pt	0.01*	0.17	0.13

*Less Than
Anion---Rem

△ Plus Anion

shipment and one from the new lot, were then submitted to an analytical testing laboratory to confirm this point. The test results show 2.9 percent calcium for the old lot and 3.3 percent calcium for the new lot. This is inconsistent with all prior spectrographic analysis. Thus far, we have submitted asbestos samples to three different laboratories for spectrographic analysis and have received a wide range of results on the major constituents. Therefore, it must be concluded that the spectrographic analysis techniques are incapable of indicating major constituent quantities of asbestos with any reasonable degree of accuracy.

Since the platinum observed is distributed in the interior of the mat as well as adjacent to the H_2 electrode, simple mechanical abrasion is not the cause for its inclusion in the mat. This conclusion is verified by the observation that only minimal platinum inclusion, due to abrasion or other mechanical modes, occurs adjacent to the O_2 electrode. The mode of platinum migration is obviously, therefore, electrochemical, but the mechanism remains a mystery.

Another approach to eliminating possible asbestos contaminants was undertaken during the last weeks of this reporting period. This consisted of acid washing the asbestos mats to remove chemically reactive species. Washing was accomplished by agitating the asbestos in glass beakers containing 20-percent HCl. During the process, the asbestos is completely shredded, losing all semblance of a flat sheet structure. After reacting for a period of 2 hours, the "mushy" asbestos is vacuum filtered using a large diameter Buchner funnel. It is then repeatedly washed (in the funnel under vacuum) with distilled water until the filtrate $pH \cong 7.0$.

After wet processing, the mats are dried and cut to 6-inch diameters. Surprisingly, the resultant mats are mechanically coherent. Tests using these matrices will be conducted early in the next reporting period.

3.3 Contaminant Studies

Researchers at the Battelle Memorial Institute have reported⁽³⁾ that caustic electrolytes, when subjected to electrolysis, yield solid electrodeposited products on the electrodes. These products are believed to be due to contaminants in the KOH. In order to verify this test result, several preliminary tests were run using our standard 40-percent KOH electrolyte. Initial screening was done in Pyrex beakers with platinum foil electrodes. Shortly after initiating electrolysis (at 80°C), a black deposit was noted on the H₂ electrode. On one test run, after a period of approximately 2 hours, a yellowish deposit was noted on the O₂ evolution electrode.

Wet analysis of the new lot of asbestos has been undertaken utilizing an analytical procedure supplied by Johns-Manville. Results obtained to date are as follows: weight loss upon ignition at 1800°F, - 17.39 percent; weight percent silicon, 18.25 percent; M_xO_y, 2.4 percent; Ca, 2.45 percent; and Mg, 22.9 percent.

American Cyanamid investigators have indicated that asbestos will dissolve in KOH at elevated temperatures. A test of fuel cell grade asbestos in excess concentrated potassium hydroxide at elevated temperatures was made to verify this point. A sample of asbestos was enclosed in a nickel screen and hung in a metal beaker containing 70 percent KOH heated at 200°C. (For a 70-percent concentration of KOH, the boiling point is slightly above 200°C.) After a period of 4 hours, the nickel screen was removed. The asbestos had entirely disappeared. This result confirms the previously reported results by American Cyanamid.⁽²⁾ A similar test at 150°C and 60-percent potassium hydroxide revealed some loss in the asbestos, but we were unable to determine the exact loss, due to shedding of the remaining material during washing after the test.

These tests were conducted with a considerable excess of electrolyte. In a fuel cell, such a dissolution process is not necessarily significant because of the minimal quantity of electrolyte used.

Wet analytical tests were conducted on samples of asbestos removed from cells that had been cycled to determine the nature of the gray-black discoloration in the asbestos mat. These samples were analyzed for platinum by dissolving the discolored asbestos in aqua regia, boiling off the nitric acid and electrodepositing the platinum from the resulting chloroplatinic acid solution on a platinum foil cathode to determine weight gain. Nonnoble materials deposited (if any) were removed by concentrated HCl immersion. In this manner, a one-square-inch sample of the asbestos mat used in cell 113 was analyzed and found to contain 15.8 milligrams of platinum. This platinum represents material that had adhered to the surface during disassembly and/or material that had migrated into the mat.

Additional tests with new solutions verified the black H₂ electrode deposits, but the yellowish deposit was not repeated. Since it is well known that hot KOH attacks Pyrex, several additional tests were made in polypropylene containers. The black H₂ electrode deposits were again found but nothing noted on the O₂ electrodes.

The chemical composition of the black deposits has not as yet been determined. However, they are soluble in HCl. Further tests will be carried out to analyze these deposits and to determine if they are due to the KOH or distilled water used in preparing the 40-percent electrolyte.

An additional spectrographic analysis was made on reaction products scraped from certain bipolar plates in cell assembly 1003-34. In appearance, this material was black and gummy, containing a quantity of moisture. The analysis showed it to be principally nickel, with a quantity of potassium (from KOH electrolyte) and a small percentage of platinum (from the electrodes). Here again is a demonstration of the conversion of nickel (from the O₂ electrode and bipolar plate) to the hydroxide as a function of cycling.

3.4 Instrumentation

Detailed wiring diagrams and equipment procurements have been prepared to expand our testing capabilities. An instrumented setup is being prepared having the capability of testing five single cells, two 6-cell units, and one 34-cell unit simultaneously. The heart of the testing complex will consist of a data acquisition system that employs a digital voltmeter, a scanner (to automatically switch the DVM to one of 100 channels), and a printer for readout of the channel being monitored. With this system, it will be possible to record continuously individual cell voltages, current, differential pressures, total pressure, and temperatures for long term cycling tests. All the components for the system have been received and the wiring for the testing of the five single cells is nearing completion. Figure 9 shows a picture of the test console. Figure 10 shows the test console with the five single cell oven test stations. Figure 11 shows a single cell test housing with the plumbing, wiring, differential, and total pressure transducers in one of the environmental ovens.

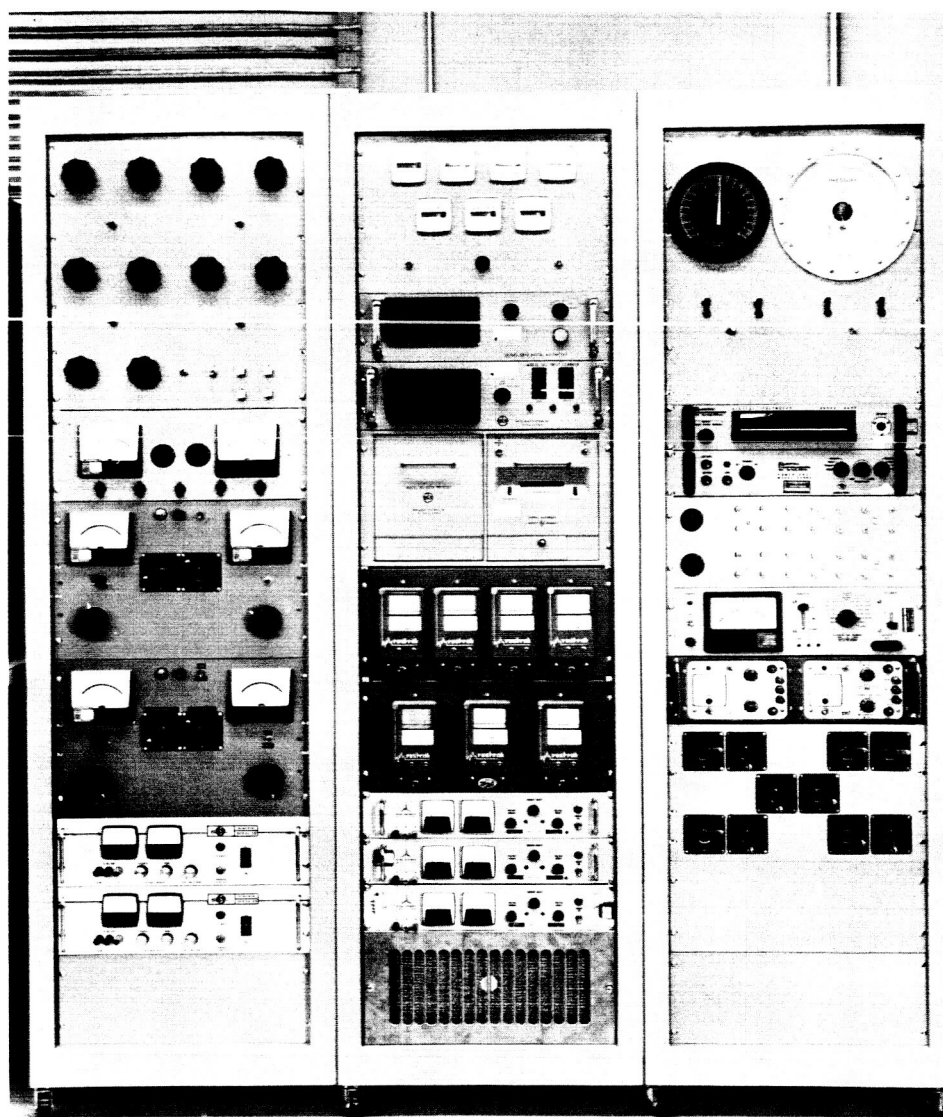


FIG. 9 FUEL CELL TEST CONSOLE

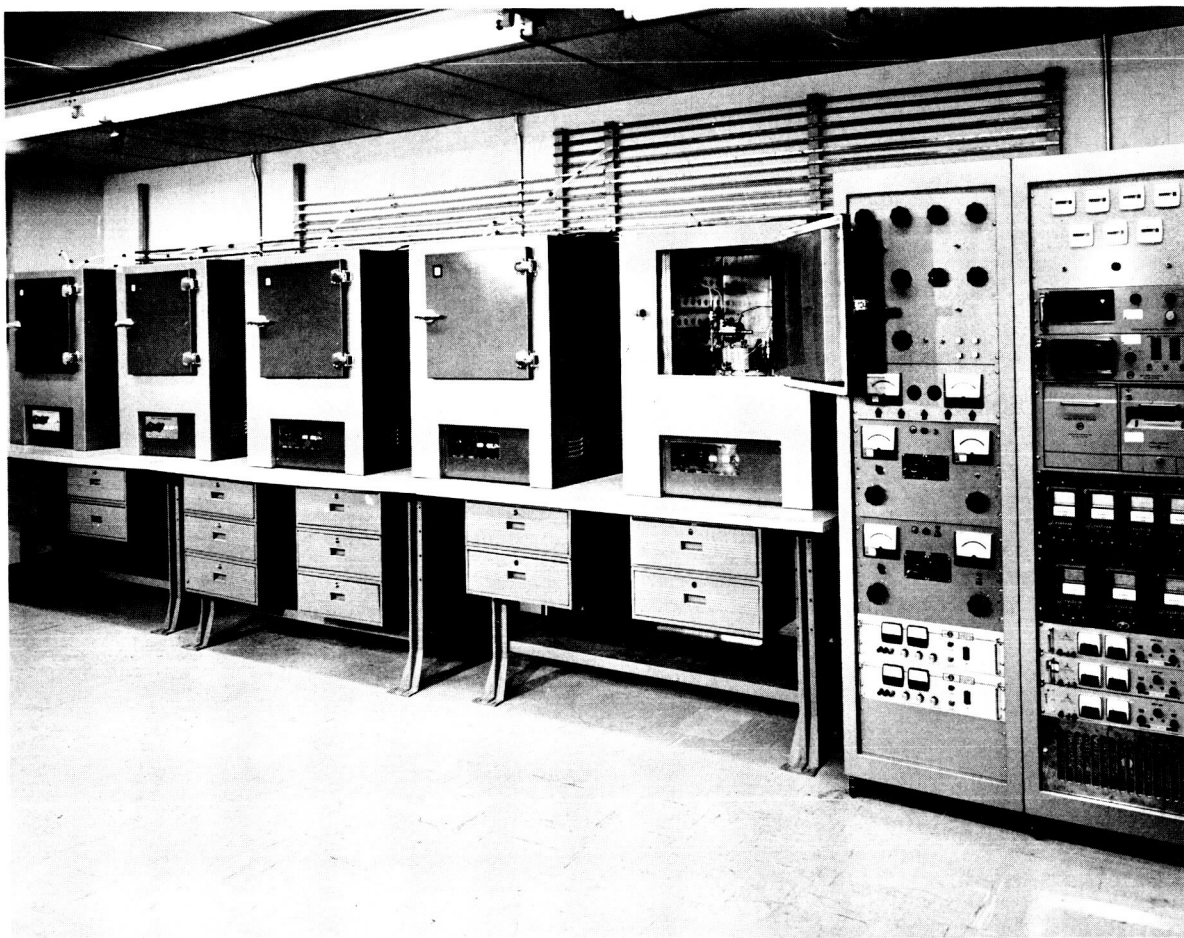


FIG. 10 FUEL CELL TEST CONSOLE AND FIVE SINGLE-CELL TEST STATIONS

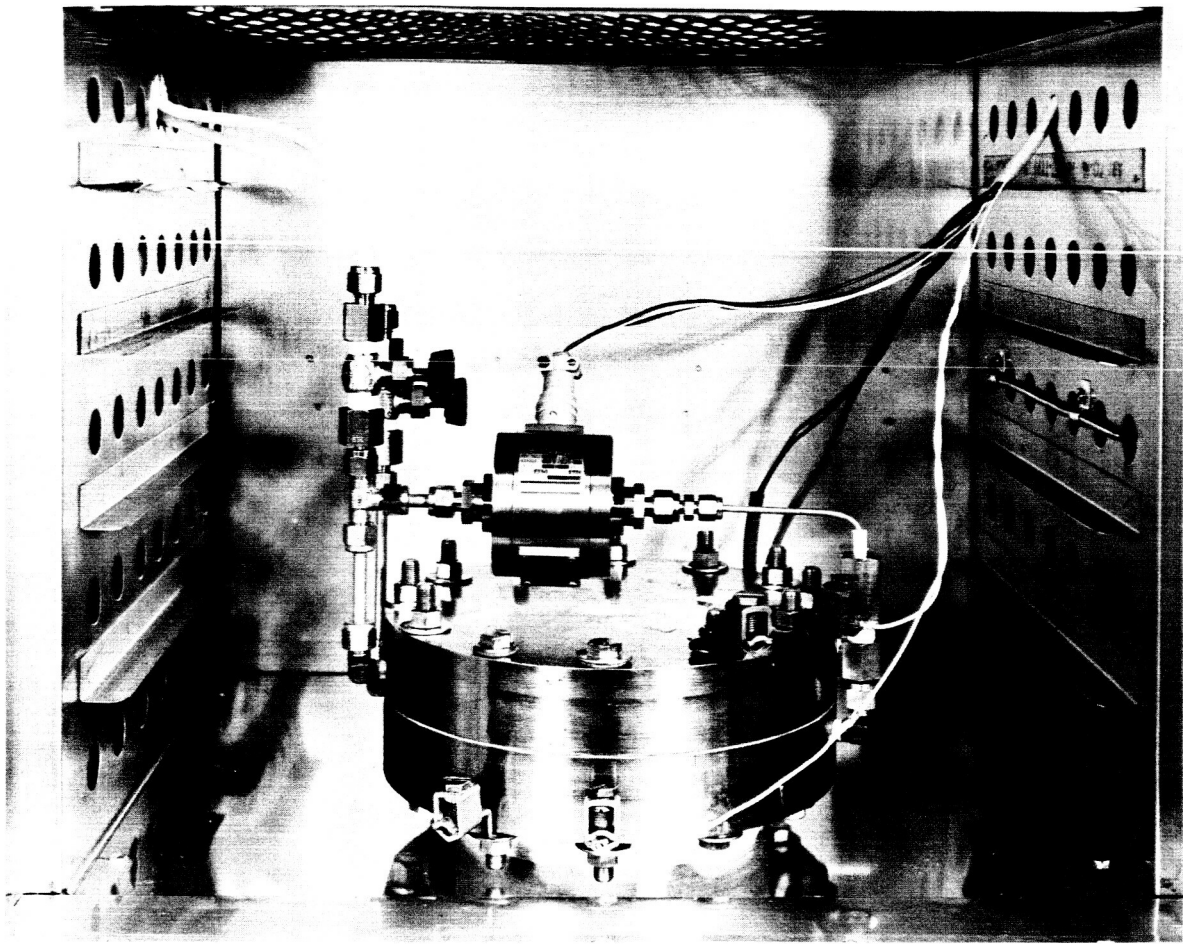


FIG. 11 SINGLE FUEL CELL TEST STATION

4. CONCLUSIONS

Testing of single cells has revealed that another mode of deterioration exists, in addition to the gradual oxidation of the nickel substrate on the oxygen electrode as previously determined. This mode of deterioration is probably due to impurities and contaminants that are contained within the asbestos mat and/or electrolyte. The coating of the porous nickel substrate by gold appears to improve the performance (at reduced catalyst loading) and reduces the rate of oxidation and degradation of the oxygen electrode.

5. PLANS FOR THE NEXT PERIOD

Single cell tests will be continued to evaluate the following oxygen electrodes:

1. American Cyanamid electrodes.
2. Porous nickel plaques that have been gold coated prior to platinization.
3. Felt metal nickel plaques that have been gold coated prior to platinization.
4. Nonsintered Teflon platinum black electrodes.

Acid washing and pretreating of the asbestos to eliminate contaminants and impurities will be investigated and promising materials will be subjected to tests in single cells. Additional studies will be conducted on the asbestos to evaluate chemical and/or electrochemical reactions that occur within cells. Impurities and contaminants in the electrolyte will be further investigated and the use of pre-electrolyzed electrolyte will be employed in single cell tests.

6. FINANCIAL STATEMENT

Manhours and dollar expenditure for the period from 3 December 1965 through 31 December 1965 were as follows:

Direct Labor Hours	637
Direct Labor Dollars	\$ 2,902.57
Purchases and Commitments	\$ 2,424.58
Total Dollar Expenditure	\$11,127.35

REFERENCES

1. M. Klein, "Hydrogen-Oxygen Electrolytic Regenerative Fuel Cells," Report No. 5, Contract NAS3-2781 (Oct. 1965)
2. W. P. Colman and J. Di Palma, "Development of High-Performance, Light Weight Electrodes for Hydrogen-Oxygen Fuel Cells," First Quarterly Report, Contract NAS3-6477 (Nov. 1965)
3. J. Clifford, E. Kolic, and C. Fanst, "Research on a Gravity Independent Water Electrolysis Cell with a Palladium Silver Alloy Cathode"